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(19) (CA) **CANADIAN PATENT** (12)

(54) Arylcarboxylic Acid Derivatives, the Preparation and Use  
Thereof

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MH 52-054

Arylcarboxylic acid derivatives, the preparation  
and use thereof

The invention relates to new compositions for combating phytopathogenic fungi, new active substances for these compositions and processes for preparing the active substances.

5

According to one feature of the invention there is provided a fungicidal composition comprising a compound of formula (I)

10



In formula I and hereinafter:

15

Aryl represents a phenyl group, either unsubstituted or mono- to tri-substituted by C<sub>1-5</sub> alkyl groups, C<sub>1-5</sub> alkoxy groups, C<sub>1-5</sub> alkyl-SO<sub>n</sub> groups wherein n represents one of the integers 0, 1 or 2, halogen atoms, groups of formula NO<sub>2</sub>, CF<sub>3</sub>, CN, CH<sub>3</sub>OCH<sub>2</sub>, (CH<sub>3</sub>)<sub>2</sub>NCH<sub>2</sub>, COOalkyl, CONH<sub>2</sub> or phenyl groups; a 1- or 2-naphthyl group; an optionally chlorine-substituted 2-, 3- or 4-pyridyl group; or a pyrimidyl or quinolyl group;

20

25

Q represents a group of formula  $\begin{array}{c} \text{R}_6 \\ | \\ \text{C} \\ | \\ \text{R}_5 \end{array} - (\text{CH}_2)_m$  wherein m is one of the integers 0, 1 and 2;

30

R<sub>1</sub> represents a hydrogen atom or a C<sub>1-5</sub> alkyl group or an allyl group,



$R_2$  and  $R_3$  independently represent hydrogen atoms,  $C_{1-6}$  alkyl groups (which may also contain an O or S atom in the chain),  $C_{3-7}$  cycloalkyl groups, phenyl groups or groups of formula  $CH_2-COO-(C_{1-5} \text{ alkyl})$ ; or  $R_2$  and  $R_3$  together represent a group of formula  $-(CH_2)_4-$ ,  $-(CH_2)_5-$ , or  $-\underset{\text{CH}_3}{\text{CH}}-(CH_2)_4-$ ;

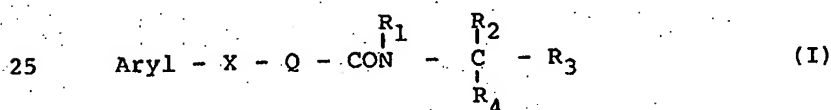
$R_4$  represents a group formula CN or  $CONH_2$ ;

$R_5$  represents a hydrogen atom or a group of formula  $CH_3$  or  $C_2H_5$ ;

$R_6$  represents a hydrogen atom or a group of formula  $CH_3$ ; and

X represents an oxygen or sulphur atom.

The majority of compounds of formula I are new and thus according to a further feature of the invention there is provided compounds of formula (I)



wherein

Aryl represents a phenyl group, either unsubstituted or mono- to tri-substituted by  $C_{1-5}$  alkyl groups,  $C_{1-5}$  alkoxy groups,  $C_{1-5}$  alkyl- $SO_n$  groups wherein n represents one of the integers 0, 1 or 2, halogen atoms, groups of formula  $NO_2$ ,  $CF_3$ , CN,  $CH_3OCH_2$ ,  $(CH_3)_2NCH_2$ , COOalkyl,  $CONH_2$  or phenyl groups; a 1- or 2-naphthyl group; an optionally chlorine-substituted

2-, 3- or 4-pyridyl group; or a pyrimidyl  
or quinolyl group;

- 5 Q represents a group of formula -  $\begin{array}{c} R_6 \\ | \\ C \\ | \\ R_5 \end{array}$  -  $(CH_2)_m$   
wherein m is one of the integers 0, 1 and 2;  
R<sub>1</sub> represents a hydrogen atom or a C<sub>1-5</sub> alkyl  
group or an allyl group,

- 10 R<sub>2</sub> and R<sub>3</sub> independently represent hydrogen atoms,  
C<sub>1-6</sub> alkyl groups (which may also  
contain an O or S atom in the chain), C<sub>3-7</sub>  
cycloalkyl groups, phenyl groups or groups  
of formula CH<sub>2</sub>-COO-(C<sub>1-5</sub> alkyl); or R<sub>2</sub> and  
15 R<sub>3</sub> together represent a group of formula  
-(CH<sub>2</sub>)<sub>4</sub>-, -(CH<sub>2</sub>)<sub>5</sub>-, or  $\begin{array}{c} -CH- \\ | \\ CH_3 \end{array} (CH_2)_4-$ ;

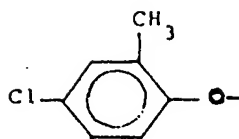
- R<sub>4</sub> represents a group formula CN or CONH<sub>2</sub>;  
20 R<sub>5</sub> represents a hydrogen atom or a group of  
formula CH<sub>3</sub> or C<sub>2</sub>H<sub>5</sub>;  
R<sub>6</sub> represents a hydrogen atom or a group of  
25 formula CH<sub>3</sub>; and

X represents an oxygen or sulphur atom;

- optionally in the form of racemates or mixtures  
30 of the optical isomers or in the form of the pure  
enantiomers or diastereomers,

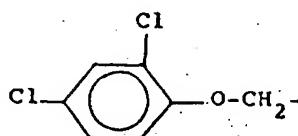
with the proviso that

- 35 (a) aryl-X- does not represent



when Q represents a group of formula  $-\text{CH}(\text{CH}_3)$   
 and  $\text{CR}_2\text{R}_3\text{R}_4$  represents a group of formula  
 10  $-\text{CH}_2\text{CN}$ ;

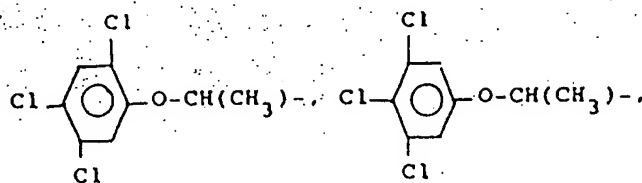
(b) aryl-X-Q does not represent

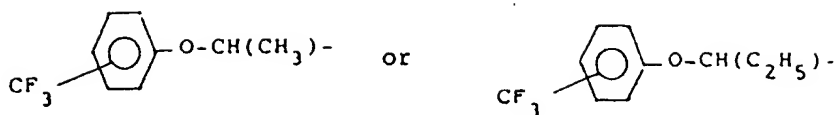


when

- 20 (1)  $\text{R}_1$  represents a hydrogen atom or  
 a  $\text{C}_{1-4}$  alkyl group and  
 (2)  $\text{R}_2$  represents a hydrogen atom or  
 a methyl or ethyl group and  
 $\text{R}_3$  represents a hydrogen atom or a methyl,  
 25 ethyl, phenyl or benzyl group or  
 $\text{R}_2$  and  $\text{R}_3$  together represent a group  
 of formula  $(\text{CH}_2)_4$  or  $(\text{CH}_2)_5$ , and  
 (3)  $\text{R}_4$  represents a group of formula  $\text{CN}$ ;

30 (c) aryl-X-Q does not represent any of the  
 following formulae





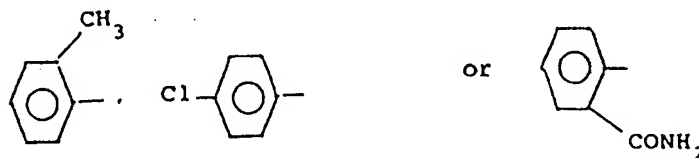
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when  $\text{CR}_2\text{R}_3\text{R}_4$  represents a group of formula  $\text{C}(\text{CH}_3)_2\text{CN}$ ; and

10

(d)  $-\text{X}-\text{Q}-\text{CONR}_1-\text{CR}_2\text{R}_3\text{R}_4$  does not represent a group of formula  $-\text{O}-\text{CH}_2-\text{CONH}-\text{CH}_2\text{CN}$  when aryl represents

15



20

The compounds of formula I may contain asymmetric carbon atoms and the invention includes the individual enantiomers of such compounds and also mixtures thereof.

25

If the substituents  $\text{R}_1$  to  $\text{R}_6$  contain hydrocarbon chains, these may be straight or branched and may be identical to or different from one another. Chains with up to 4, more particularly up to 3 carbon atoms are preferred. The preferred alkyl substituent in the aryl group is a methyl group. Halogen atoms include fluorine, chlorine, bromine and iodine, preferably chlorine or fluorine. The substituents in the aryl group may be identical or different although the groups of formulae  $\text{CF}_3$ ,  $\text{CN}$ ,  $\text{NO}_2$ ,  $(\text{CH}_3)_2\text{NCH}_2$  and  $\text{C}_{1-5}$  alkyl- $\text{SO}_n$  and the phenyl group generally occur only once. If aryl

30

35

represents a quinolinyl group it is preferably an 8-quinolinyl group.

The compounds of formula (I) may be prepared by several processes and these processes from a still further feature of the invention. These processes include:

1. reaction of a compound of formula (II)

10



wherein aryl, X and Q are as hereinbefore defined and Y represents a leaving group, e.g. a halogen atom (preferably chlorine), or an alkoxy, hydroxy or acyl group, with a compound of formula (III)

15

20



wherein  $\text{R}_1 - \text{R}_4$  are as hereinbefore defined, thereby eliminating  $\text{HY}$ ; and

25

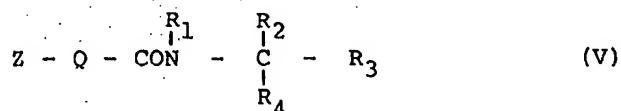
2. reaction of a compound of formula (IV)



30

wherein aryl and X are as hereinbefore defined and M indicates a hydrogen atom or an alkali metal cation, with a compound of formula (V)

35





wherein  $R_1$  to  $R_4$  and  $Q$  are as hereinbefore defined and  $Z$  represents a halogen atom or an arylsulphonyloxy group.

5

The reaction of type (1) is preferably carried out in an inert solvent, e.g. methylene chloride, toluene, acetonitrile, an ether, or in a mixture of solvents at temperatures between ambient temperature and the boiling temperature of the reaction mixture; the reaction will be promoted if an HY-binding agent is present, for example a base if HY represents an acid such as HCl, or dicyclohexylcarbodiimide or carbonyldiimidazole if HY represents water.

15

The starting materials of formula (II) are known compounds or may easily be prepared by conventional methods. Thus compounds of formula (II) wherein  $Y = OH$  may be obtained for example by reaction of a suitable phenol or thiophenol (aryl-XH) with an ester of a suitable bromosubstituted carboxylic acid in the presence of a base and subsequent hydrolysis of the ester. From the carboxylic acids thus obtained, the corresponding carboxylic acid chlorides of formula (II) are formed, e.g. by reacting with thionyl chloride.

The  $\alpha$ -amino acid nitriles (compounds of formula (II) wherein  $R_4 = CN$ ), may be prepared by Strecker synthesis from the corresponding ketone or aldehyde, NaCN and  $NH_4Cl$  in water (see Houben-Weyl, Vol. VIII, page 274ff (1952)). The  $\alpha$ -amino acid amides (compounds of formula (III) wherein  $R_4 = CONH_2$ ) are obtained from the corresponding nitriles by partial hydrolysis.

The reaction of type (2) may be carried out in an inert polar solvent. If  $M = H$ , a base is desirably added. Conditions under which a compound of formula (IV) wherein  $M = K$  or  $Na$  is formed are preferred.

5

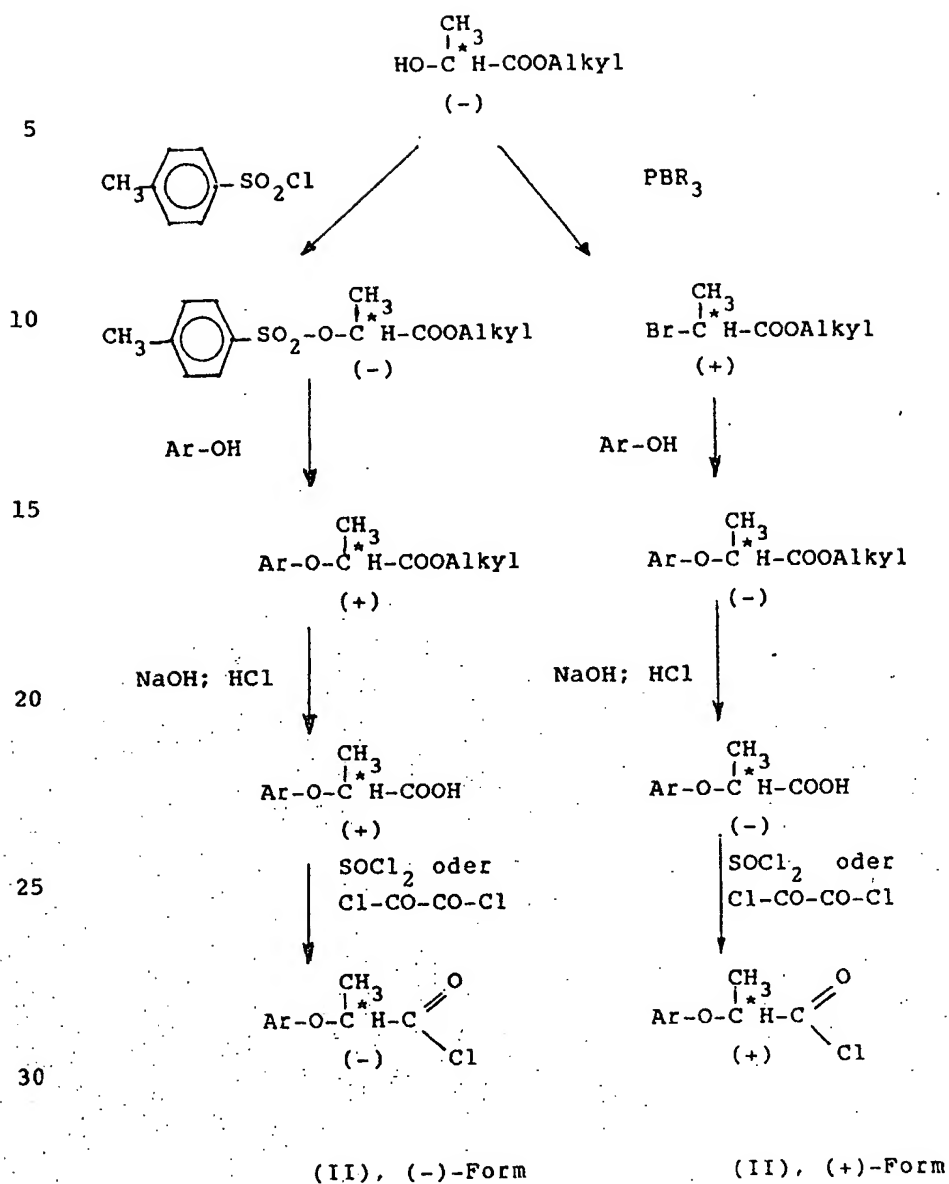
The preferred definitions of  $Z$  in formula (V) are a bromine atom or a group of formula  $CH_3-C_6H_4-SO_3^-$  whilst the preferred solvent is acetonitrile.

The reaction is generally carried out at elevated temperatures, e.g. at reflux temperature. Suitable bases include, for example, alkali metal carbonates, alkali metal hydroxides, and optionally also sufficiently basic amines such as triethylamine.

15 Depending on the definitions of  $R_2$  to  $R_6$ , compounds of formula I with one or two centres of asymmetry may occur. The isomers may, if desired, be separated by conventional methods or synthesised directly by using optically active starting products.

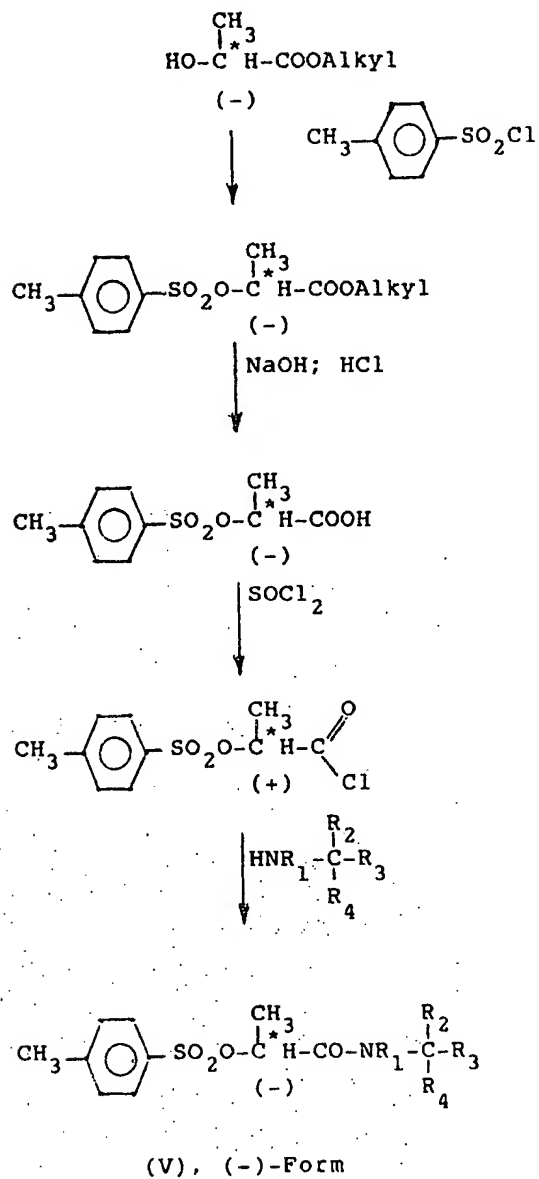
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Two methods of preparing optically active compounds of formula (II) from an optically active  $\alpha$ -hydroxy acid ester are illustrated below (the asymmetric carbon is marked with an asterisk):



35 "Alkyl" preferably represents methyl or ethyl.  
Other compounds of formula (II) may be prepared  
according to the same general scheme.

Similar steps lead to optically active starting materials of formula (V); in this case, too, other optically active compounds of formula (V) may be obtained accordingly.



The compounds of formula I have a fungitoxic effect on phytopathogenic fungi, and accordingly methods of preventing and/or combating fungal infections in plants form a yet further feature of the invention. The compounds may be used particularly against  
5 fungal diseases in rice, for instance Piricularia.

Although the new compounds are partly derived from herbicides (Dichlorprop, 2,4-DB) they are surprisingly well tolerated by plants.

10 To prepare the fungicidal compositions according to the invention the compounds of formula (I) are processed with conventional excipients and/or carriers to produce the usual preparations, which may be  
15 diluted for use in the form of a spray liquor with suitable quantities of water. Preparations of this kind include, for example, emulsifiable and soluble concentrates, wettable powders, dusting powders and granules which may contain up to 80%  
20 by weight of active substance.

The activity of the compounds according to the invention, e.g. against Piricularia, was tested on rice seed under tropical conditions. 2 rows  
25 of rice seed (I and II) between older rows naturally infected with Piricularia were treated on the 41st, 45th and 49th day after sowing with spray liquors containing specific quantities of active substance. A control treated only with water was used as a  
30 comparison. The results were graded 6, 8, 10 and 13 days after the last spraying (expressed as a % of plants attacked).

The compounds according to the invention proved  
35 highly effective against Piricularia and well tolerated by the plants.

Additional tests are described hereinafter.

Effect against Piricularia in riceA. Leaf treatment

- 5 Rice plants were first grown in propagation trays. They were sprayed until dripping wet with emulsions or suspensions containing 1000, 500 or 250 ppm of the active substance in question. Two days after treatment the propagation trays were left
- 10 in the open between infected rice plants for 5-6 days to allow infection to occur. Findings were evaluated 5-8 days later.

B. Soil treatment

- 15 Rice plants were first grown in flower pots. Emulsions or suspensions containing 500 ppm of the active substances specified were poured onto the roots. Two days after treatment the pots were left in
- 20 the open for 4-6 days between rice plants infected with Piricularia in order to allow infection to occur. The results were evaluated 5-7 days after the infection.

- 25 The findings were graded 1 to 3:

- 1: no attack  
2: slight attack  
3: attack similar to that of the untreated control.

30

The numbers given in Table A hereinafter are averages from 3 tests and several grades awarded at different times.

C. Application under water (submerged application)

Rice plants were planted in earth-filled buckets. Water was added until it formed an unbroken covering over the earth. A quantity of active substance was added in the form of a suspension or emulsion to correspond to an application of 8 or 4 or 2 kg/ha active ingredient. Two days after treatment the test plants were left in the open between infested rice plants and remained exposed to infection throughout the experiment. The results were evaluated one day after attack had occurred on the untreated control and the evaluation was carried out 4-5 times (3 experiments with each substance). Evaluation was as in A and B. The numbers in the table are the averages from three experiments and several grades awarded at different times as the experiment progressed.

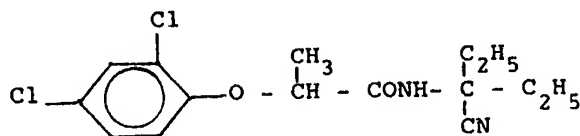
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Table A: Test results

Active substance according to Example:	Concentration of active substance [ppm]	Number of attacks		Test C	
		Test A	Test B	kg/ha	Number of Attacks
Tab. II No. 62	1000 500 250	1.0 1.0 1.0	1.8	8	2.0
Example No. 9	1000 500 250	1.0 1.0 1.5	2.0	4 2	1.8 2.2
Tab. II No. 1	1000 500 250	- 1.0 1.0	2.5	8	1.8
Tab. V No. 2	1000 500 250	1.0 1.5 2.5	1.0	4	1.5
Example No. 4	1000 500 250	1.0 1.8 2.1	2.1	8	1.8
Tab. II No. 2	1000 500 250	1.1 1.0 2.0	-	4	2.0
Tab. II No. 33	1000 500 250	1.0 1.0 2.0	-		
Example No. 6e	1000 500 250	1.5 2.0 2.0	2.0		
Tab. IV No. 6	1000 500 250	- 1.0 1.0	1.9		



Example 12-(2,4-Dichlorophenoxy)-propionic acid-N-(1-ethyl-1-cyanopropyl)-amide

10

2.2 g of 3-amino-3-cyanopentane and 2.4 g of triethylamine are dissolved in 100 ml of methylene chloride.

5.1 g of 2-(2,4-dichlorophenoxy)-propionic acid chloride are added and the mixture is stirred overnight

15 at ambient temperature. The solution is extracted with water and sodium hydrogen carbonate solution,

dried and evaporated down. The residue obtained consists of 6.3 g (96% of theory) of a brownish viscous oil which crystallises when stirred with

20 diisopropylether.

Yield: 4.9 g of white solids (74% of theory)

Melting point: 100 - 102°C

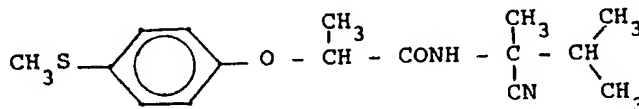
25 The structure is confirmed by spectroscopic investigation.

Analysis:  $C_{15}H_{18}Cl_2N_2O_2$   $M = 329.23$

	C%	H%	Cl%	N%
30 Found:	54.58	5.54	21.06	8.35
Calculated:	54.72	5.51	21.54	8.51

Example 22-(4-Methylthiophenyloxy)-propionic acid-N-(1-cyano-1,2-dimethylpropyl)-amide

5



10

2.5 g of 2-bromopropionic acid-N-(1-cyano-1,2-dimethylpropyl)-amide (prepared analogously to Example 5a) and 1.4 g of 4-methylmercaptophenol are dissolved in 50 ml of methylisobutylketone. After the addition of 1.5 g of potash the mixture is stirred for 3 hours at 80°C. The solution is suction filtered and evaporated down. 2.8 g of brownish oil are obtained (91.5%) which crystallises when stirred with diisopropylether.

M.p. 83-86°C

Analysis:  $C_{16}H_{22}N_2O_2S$   $M = 306.43$

25

	C%	H%	N%	S%
Found:	62.48	7.24	9.23	10.34
Calculated:	62.71	7.24	9.14	10.46

The structure was confirmed by spectroscopy.

30

Example 32-(4-Chloro-2-methylphenoxy)-propionic acid-N-[3-cyanopent-3-yl]-amide

35

4.4 g of 2-amino-2-ethylbutyronitrile (0.039 mol) and 4.6 g of triethylamine (0.046 mol) are dissolved

in methylene chloride, 9.0 g of 2-(4-chloro-2-methyl-  
phenoxy)-propionic acid chloride (0.039 mol) are  
added dropwise with stirring. The mixture heats  
up. It is stirred for a further 3 hours without  
5 heating, extracted successively with water and  
bicarbonate solution, then dried and evaporated  
down. The residue obtained consists of a brown  
oil (10.8 g) which crystallises when stirred with  
isopropylether. The product is suction filtered  
10 and dried.

Yield: 10.6 g (88% of theory) of white solids  
M.p.: 125 - 126°C.

15 Elemental analysis and NMR spectrum confirm the  
formula given.

Example 4

20 2-(4-Chloro-2-methylphenoxy)-propionic acid-N-[2-  
cyano-3-methylbut-2-yl]-amide

Analogously to Example 3 the title compound is  
obtained from equimolar quantities of 2-amino-2,3-  
25 dimethylbutyronitrile.

Yield: 76% of theory; m.p.: 97 - 99°C.

The product is initially obtained as a brown oil.  
30 It consists of 4 isomers. The mixture can be resolved  
into 3 fractions by step-wise precipitation with  
cold ether.

From 11.1 g of oil are obtained:

35

Fraction I: 1.8 g of white solids  
m.p.: 117-118°C;

Fraction II: 1.8 g of brownish solids

m.p.: 94-96°C;

Fraction III: 5.6 g of reddish oil (purified by chromatography)

5

NMR spectroscopy indicates enrichment of the pairs of enantiomers in Fractions I and II:

10      Fraction I      Enantiomeric pair I to enantiomeric  
pair II 89 : 11 (diastereomeric ratio)

Fraction II      Enantiomeric pair I to enantiomeric  
pair II 26 : 74

15

The pairs of enantiomers may be further concentrated by recrystallising the fractions.

The following compounds of the general formula given below were also obtained in accordance with the preceding Examples:

5

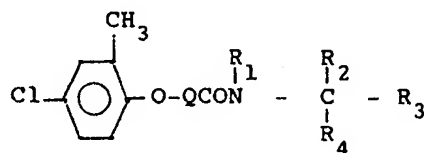


Table I

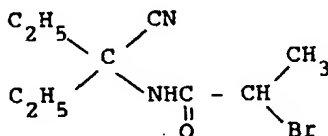
No.	Q	R <sub>2</sub>	R <sub>3</sub>	R <sub>1</sub>	R <sub>4</sub>	M p. [°C]
1	CH <sub>2</sub>	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	H	CN	86-88
2	CH(CH <sub>3</sub> )	i-C <sub>3</sub> H <sub>7</sub>	CH <sub>3</sub>	H	CONH <sub>2</sub>	108-111
3	CH <sub>2</sub>	i-C <sub>3</sub> H <sub>7</sub>	CH <sub>3</sub>	H	CONH <sub>2</sub>	105-107
4	CH <sub>2</sub>	i-C <sub>3</sub> H <sub>7</sub>	CH <sub>3</sub>	H	CN	102-103
5	CH(CH <sub>3</sub> )	n-C <sub>3</sub> H <sub>7</sub>	CH <sub>3</sub>	H	CN	71-75
6	CH(CH <sub>3</sub> )	C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>	H	CN	86-87
7	CH(CH <sub>3</sub> )	n-C <sub>3</sub> H <sub>7</sub>	CH <sub>3</sub>	H	CONH <sub>2</sub>	100-102
8	CH(CH <sub>3</sub> )	n-C <sub>5</sub> H <sub>11</sub>	CH <sub>3</sub>	H	CN	
9	CH(CH <sub>3</sub> )	-(CH <sub>2</sub> ) <sub>5</sub> -		H	CN	134-136
10	CH <sub>2</sub>	-(CH <sub>2</sub> ) <sub>5</sub>		H	CN	118-120
11	CH <sub>2</sub>	i-C <sub>3</sub> H <sub>7</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CN	
12	CH(CH <sub>3</sub> )	i-C <sub>3</sub> H <sub>7</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CN	Oil
13	CH(CH <sub>3</sub> )	-(CH <sub>2</sub> ) <sub>4</sub> -		H	CN	143-146
14	CH(CH <sub>3</sub> )	-CH-(CH <sub>2</sub> ) <sub>4</sub>   CH <sub>3</sub>		H	CN	121-127

Example 52-(4-Chlorophenylthio)-propionic acid-N-(1-ethyl-1-cyanopropyl)-amide

5

a) 2-Bromopropionic acid-N-(1-ethyl-1-cyanopropyl)-amide

10



15

36.5 g of 2-amino-2-cyano-n-pentane in 100 ml of methylene chloride are added dropwise, with stirring, over a period of 40 minutes, to 88.4 g of 2-bromopropionic acid anhydride (0.325 mol) dissolved in 280 ml of methylene chloride.

20

After stirring overnight, the solution is extracted with water and sodium bicarbonate solution, dried and evaporated down. The remaining oil is triturated with a little ether whereupon the product crystallises out.

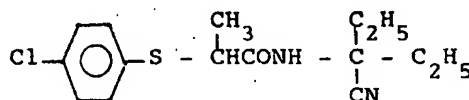
25

M.p. 85-87°C

Yield: 61.2 g (76.5% of theory)

b)

30



35

5.8 g of 4-chlorothiophenol (0.04 mol) are stirred in 150 ml of methylisobutylketone with 12.2 g of potassium carbonate at 90°C for 10 minutes. 9.9 g of 2-bromopropionic acid-N-(1-ethyl-1-

cyanopropyl)-amide are added to the resulting suspension with stirring and the mixture is stirred for another 5 hours at about 90°C. The solution is filtered, extracted successively

5 with water, 2N sodium hydroxide solution and water, dried with magnesium sulphate and evaporated down. A brown oil is obtained which hardens to form a brownish crystalline mass when stirred with a little ether.

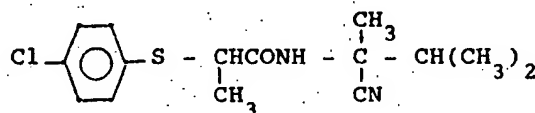
10 M.p. 108-110°C

Yield: 7.2 g (58.1% of theory)

#### Elemental analysis

15	C	H	N	Cl	S
	Calc.: 57.96%	6.16%	9.01%	11.4%	10.32%
	Found: 57.77%	6.35%	8.86%	11.32%	10.28%

The following compound is also obtained according to the preceding Example



25 M.p.: 106-109°C.

#### Example 6

30 (+)-2-(4-Chloro-2-methylphenoxy)-propionic acid-N-(1-ethyl-1-cyanopropyl)-amide

a) Methyl (-)-O-(4-methylphenylsulphonyl)-lactate

35 26.9 g of triethylamine are added dropwise to a solution of 25.2 g of methyl S-(-)-lactate and 46.1 g of p-toluenesulphonic acid chloride

in 160 ml of toluene. The mixture is stirred overnight and the precipitate is removed by suction filtering. The toluene solution is extracted with dilute hydrochloric acid and water, dried with sodium sulphate and evaporated down. 55.9 g of colourless oil are obtained, which is purified by vacuum distillation.

B.p.<sub>0.2</sub>: 148-152°C [ $\alpha$ ]<sub>D</sub><sup>24</sup>: -50.1° (ethanol)  
yield: 43.5 g (70% of theory)

b) Methyl (+)-(4-chloro-2-methylphenoxy)-propionate

41.9 g of methyl S-(-)-O-(4-methylsulphonyl)-lactate and 23.1 g of 4-chloro-2-methylphenol are dissolved in 100 ml of acetonitrile, 50 g of potash are added and the mixture is refluxed for 10 hours with stirring. The solution is suction filtered and evaporated down. The residue is taken up in toluene, extracted with 1N sodium hydroxide solution, dried and concentrated by evaporation. 32.2 g of reddish liquid are obtained (87% of theory)

c) (+)-4-Chloro-2-methylphenoxypropionic acid

The crude product obtained in b) (32.2 g) is dissolved in 100 ml of acetone. A solution of 6.8 g of NaOH in 30 ml of water is added dropwise with stirring and while cooling with ice. After stirring overnight the mixture is diluted with water and extracted with methylene chloride. The aqueous solution is acidified with conc. hydrochloric acid and the product precipitated is extracted with methylene chloride. The methylene chloride solution is separated off, dried and evaporated down. An oily residue is obtained which solidifies immediately.



M.p.: 62-72°C (pressed onto clay)

$[\alpha]_D^{24}$ : + 14.1° (ethanol)

Yield: 27.7 g (91% of theory)

5 d) (-)-4-Chloro-2-methylphenoxypropionic acid chloride

27.2 g of (+)-4-chloro-2-methylphenoxypropionic acid and 30.2 g of thionyl chloride are stirred with 100 ml of toluene for 3 hours at 100°C.

10 The solution is evaporated down in vacuo. 29.6 g of brown oil are obtained, which is reacted without purification.

15 e) (+)-2-(4-Chloro-2-methylphenoxy)-propionic acid-N-(1-ethyl-1-cyanopropyl)-amide

8.4 g of the crude product from d) are added dropwise to 4 g of 3-amino-3-cyano-n-pentane and 4.4 g of triethylamine, dissolved in 100 ml of toluene, at -20 to -30°C with stirring.  
20 The mixture is then stirred for 3 hours at RT, extracted with water and the solution is evaporated down. The oily residue (8.8 g) is stirred with diisopropylether, whereupon a crystalline product  
25 is precipitated and then separated off.

Yield: 2.8 g (25% of theory)

M.p.: 98-100°C

$[\alpha]_D^{22}$ : + 9.1° (ethanol)

Example 7(-)-2-(4-Chloro-2-methylphenoxy)-propionic acid-  
N-(1-ethyl-1-cyanopropyl)-amide

5

## a) Ethyl (+)-2-bromopropionate

47.2 g of ethyl S-(-)-lactate are dissolved  
in 300 ml of methylene chloride. 108 g of phosphorus  
10 tribromide are added dropwise. The reaction  
is exothermic. After stirring overnight at  
RT the mixture is poured onto ice and stirred  
with water. The methylene chloride solution  
is extracted with bicarbonate solution, dried  
15 and evaporated down. The residue is distilled.  
Yield: 33.8 g; colourless oil (47% of theory)  
BP<sub>25</sub> mbar 55-56°C.

## 20 b) Ethyl (-)-(4-chloro-2-methylphenoxy)-propionate

The product described in a) (33.8 g) is dissolved  
together with 26.7 g of 4-chloro-2-methylphenol  
in 300 ml of toluene and after the addition  
of 52 g of K<sub>2</sub>CO<sub>3</sub> it is refluxed for 10 hours  
25 with stirring. The solution is suction filtered,  
extracted twice with 1N sodium hydroxide solution,  
dried and evaporated down. 34.3 g of clear  
liquid are obtained (76% of theory)  
[α]<sub>D</sub><sup>22</sup>: -14.46° (ethanol)

30

c) (-)-(4-Chloro-2-methylphenoxy)-propionic acid  
(-)-CMPP

Hydrolysis of the ester obtained in b) is carried  
out as in Example 6c).  
35 From 24.2 g of ethyl (-)-(4-chloro-2-methylphenoxy)-  
propionate, 19.7 g of (-)-(4-chloro-2-methylphenoxy)-  
propionic acid are obtained (92% of theory).

M.p.: 69-75°C

$[\alpha]_D^{22}$ : -9.679° (ethanol)

- 5 d) (+)-(4-Chloro-2-methylphenoxy)-propionic acid  
chloride  
(+)-CMPP-chloride)  
The acid described in 7c) is converted analogously  
to Example 6d) into the acid chloride which  
is further processed without purification.  
10 From 8.6 g of (-)-CMPP, 8.4 g of (+)-CMPP chloride  
is obtained as a brownish oil (90% of theory)  
 $[\alpha]_D^{22}$ : +4.486° (CCl<sub>4</sub>)

- 15 e) (-)-2-(4-Chloro-2-methylphenoxy)-propionic acid-  
N-(1-ethyl-1-cyanopropyl)-amide

The (+)-CMPP chloride is reacted with 3-amino-  
3-cyano-n-pentane as described in Example 6e).  
3 g of (-)-2-(4-chloro-2-methylphenoxy)-propionic  
20 acid-N-(1-ethyl-1-cyanopropyl)-amide are obtained  
(28% of theory) from 8 g of (+)-CMPP chloride.  
M.p.: 98-100°C  
 $[\alpha]_D^{22}$ : -8.584° (ethanol)

- 25 A variant for the preparation of the dextrorotatory  
phenoxypropionic acid amides is described hereinafter  
taking as an example (+)-2-(4-chloro-2-methylphenoxy)-  
propionic acid-N-(1-ethyl-1-cyanopropyl)-amide:

30 Example 8

(+)-2-(4-Chloro-2-methylphenoxy)-propionic acid-  
N-(1-ethyl-1-cyanopropyl)-amide

- 35 a) (+)-O-(4-Methylphenylsulphonyl)-lactic acid  
chloride

17.9 g of (-)-O-(4-methylphenylsulphonyl)-lactic acid (Helv. Chim. Acta 65/1240 (1982)) and 13 g of thionyl chloride are stirred at 95-100°C for 3 hours. The product is evaporated down  
5 in vacuo and degassed. 19.2 g of brown oil are obtained (100% of theory).

b) (-)-O-(4-Methylsulphonyl)-lactic acid-N-(1-ethyl-1-cyanopropyl)-amide

10

18.8 g of the crude product from 8a) are added dropwise at -20 to -30°C to a solution of 8 g of 3-amino-3-cyano-n-pentane and 8.8 g of triethylamine in 200 ml of toluene. The mixture is  
15 stirred for 3 hours at -20°C and then overnight at RT. The solution is extracted with water and evaporated down. 23.4 g of brown clear oil are obtained (96% of theory) which is crystallised by stirring with diisopropylether.

20 M.p.: 57-60°C  $[\alpha]_D^{22}$  -40.4° (ethanol)  
Yield: 8.4 g (34% of theory)

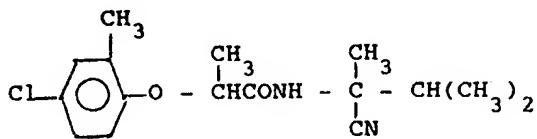
c) (+)-2-(4-Chloro-2-methylphenoxy)-propionic acid-N-(1-ethyl-1-cyanopropyl)-amide

25

4.7 g of (-)-O-(4-methylsulphonyl)-lactic acid N-(1-ethyl-1-cyanopropyl)-amide and 2 g of 4-chloro-2-methylphenol are dissolved in 100 ml of toluene. 4.5 g of powdered potash are added  
30 and the mixture is refluxed for 12 hours with stirring. The solution is suction filtered, extracted with 1N sodium hydroxide solution and evaporated down. 3.1 g of yellow oil are obtained (72% of theory) which crystallises  
35 when stirred with diisopropylether. 2.2 g of white crystalline solids are obtained (51% of theory).  
M.p.: 97-99°C  $[\alpha]_D^{22}$  : +11.94° (ethanol)

In accordance with Examples 6 to 8, the dextro- and levorotatory enantiomers of the following compound are also prepared:

5



10

Example 9:  $[\alpha]_D^{22} = 9.1^\circ$

(ethanol) oils, mixtures of diastereomers

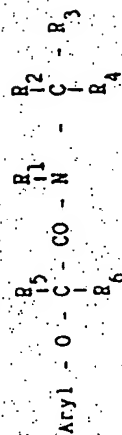
15 Example 10:  $[\alpha]_D^{22} = -7.65^\circ$


(ethanol)

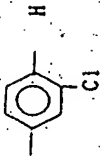
The following compounds, listed in Tables II to IX, were prepared by analogous methods.


TABLE II

Compounds of formula

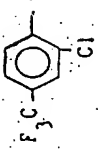
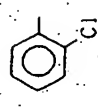
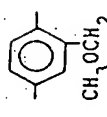
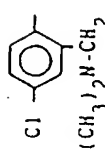
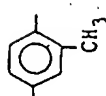


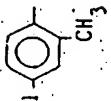
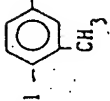
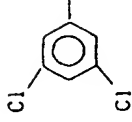
No. Aryl	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	R <sub>5</sub>	R <sub>6</sub>	M P (°C)	
1		H	CH <sub>3</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>	CN	H	CH <sub>3</sub>	79-80
2	"	H	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	CN	H	CH <sub>3</sub>	105-107
3	"	CH <sub>3</sub>	CH <sub>3</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>	CN	H	CH <sub>3</sub>	Oil
4	"	H	-(CH <sub>2</sub> ) <sub>5</sub> -	CN	H	CH <sub>3</sub>	142-144	
5	"	H	CH <sub>3</sub>	n-C <sub>8</sub> H <sub>17</sub>	CN	H	CH <sub>3</sub>	65-67
6	"	H	CH <sub>3</sub>	CH <sub>2</sub> CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	CN	H	CH <sub>3</sub>	74-76

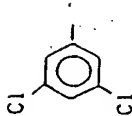
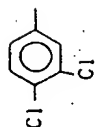
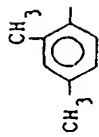
No. Aryl	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	R <sub>5</sub>	R <sub>6</sub>	M P (°C)
7		C <sub>2</sub> H <sub>5</sub>	CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	CN	H	CH <sub>3</sub>	70-75
8	"	CH <sub>3</sub>	CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	CN	H	CH <sub>3</sub>	74-75
9	"	H	-(CH <sub>2</sub> ) <sub>4</sub>	CN	H	CH <sub>3</sub>	117-119
10	"	H	CH(CH <sub>3</sub> ) <sub>2</sub>	CN	H	CH <sub>3</sub>	Oil
11	"	CH <sub>3</sub>	-CH <sub>2</sub> OCH <sub>3</sub>	CN	H	CH <sub>3</sub>	Oil
12	"	H	-CH(CH <sub>3</sub> )-(CH <sub>2</sub> ) <sub>4</sub>	CN	H	CH <sub>3</sub>	129-134
13	"	CH <sub>3</sub>	-CH <sub>2</sub> COOC <sub>2</sub> H <sub>5</sub>	CN	H	CH <sub>3</sub>	

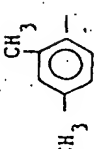
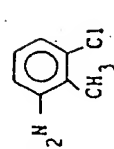

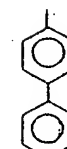
No.	Aryl	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	R <sub>5</sub>	R <sub>6</sub>	Mp (°C)
14		H	CH <sub>3</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>	CN	H	H	85-87
15		H		-(CH <sub>2</sub> ) <sub>5</sub> -	CN	H	H	94-96
16	"	H	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	CN	H	H	50-52
17	"	H	CH <sub>3</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>	CN	H	CH <sub>3</sub>	80-81
18	"	CH <sub>3</sub>	CH <sub>3</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>	CN	H	CH <sub>3</sub>	Oil
19	"	H	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	CN	H	CH <sub>3</sub>	83-84
20	"	H	CH <sub>3</sub>	n-C <sub>5</sub> H <sub>11</sub>	CN	H	CH <sub>3</sub>	75-77
21	"	H	CH <sub>3</sub>	CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	CN	H	CH <sub>3</sub>	58-62


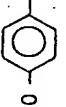

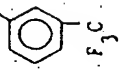


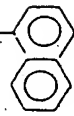






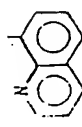
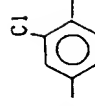
No. Aryl	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	R <sub>5</sub>	R <sub>6</sub>	M p (°C)	
22	C <sub>6</sub> H <sub>5</sub>	H	CH <sub>3</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>	CN	H	CH <sub>3</sub>	81-83
23		H	CH <sub>3</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>	CN	H	CH <sub>3</sub>	120-124
24		H	CH <sub>3</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>	CN	H	CH <sub>3</sub>	60-62
25	"	H	CH <sub>3</sub>	n-C <sub>5</sub> H <sub>11</sub>	CN	H	CH <sub>3</sub>	97-100
26		H	CH <sub>3</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>	CN	H	CH <sub>3</sub>	Oil
27		H	CH <sub>3</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>	CN	H	CH <sub>3</sub>	Oil
28		H	CH <sub>3</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>	CN	H	C <sub>2</sub> H <sub>5</sub>	98-100

No.	Ar	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	R <sub>5</sub>	R <sub>6</sub>	Mp (°C)
29		H	CH <sub>3</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>	CN	CH <sub>3</sub>	CH <sub>3</sub>	94-97
30		H	CH <sub>3</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>	CN	H	CH <sub>3</sub>	110
31	"	H	CH <sub>3</sub>	n-C <sub>5</sub> H <sub>11</sub>	CN	H	CH <sub>3</sub>	Oil
32	"	H	CH <sub>3</sub>	CH(CH <sub>3</sub> ) <sub>3</sub>	CONH <sub>2</sub>	H	CH <sub>3</sub>	155
33		H	CH <sub>3</sub>	CH(CH <sub>3</sub> ) <sub>3</sub>	CN	H	CH <sub>3</sub>	105
34	"	H	CH <sub>3</sub>	CH(CH <sub>3</sub> ) <sub>3</sub>	CONH <sub>2</sub>	H	CH <sub>3</sub>	140

No. Aryl	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	R <sub>5</sub>	R <sub>6</sub>	Mp (°C)	
35		H	CH <sub>3</sub>	n-C <sub>5</sub> H <sub>11</sub>	CN	H	CH <sub>3</sub>	Oil
36		H	CH <sub>3</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>	CN	H	CH <sub>3</sub>	103
37	"	H	CH <sub>3</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>	CONH <sub>2</sub>	H	CH <sub>3</sub>	150
38	"	H	CH <sub>3</sub>	n-C <sub>5</sub> H <sub>11</sub>	CN	H	CH <sub>3</sub>	Oil
39		H	CH <sub>3</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>	CN	H	CH <sub>3</sub>	106
40	"	H	CH <sub>3</sub>	n-C <sub>3</sub> H <sub>7</sub>	CN	H	CH <sub>3</sub>	142

NO.	Acyl	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	R <sub>5</sub>	R <sub>6</sub>	Mp (°C)
41		H	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	CN	H	CH <sub>3</sub>	114
42	"	H	-(CH <sub>2</sub> ) <sub>5</sub>		CN	H	CH <sub>3</sub>	121
43	"	CH <sub>3</sub>	CH <sub>3</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>	CONH <sub>2</sub>	H	CH <sub>3</sub>	85-90
44		H	CH <sub>3</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>	CN	H	CH <sub>3</sub>	160
45	"	H	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	CN	H	CH <sub>3</sub>	152-154
46		H	CH <sub>3</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>	CN	H	CH <sub>3</sub>	88-90
47		H	CH <sub>3</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>	CN	H	CH <sub>3</sub>	106-108

No. Acyl	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	R <sub>5</sub>	R <sub>6</sub>	M p (°C)
48		H	CH <sub>3</sub>	CN	H	CH <sub>3</sub>	98-100
49		H	CH <sub>3</sub>	CN	H	CH <sub>3</sub>	57-63
50		H	C <sub>2</sub> H <sub>5</sub>	CN	H	CH <sub>3</sub>	
51		H	CH <sub>3</sub>	CN	H	CH <sub>3</sub>	78-81
52		H	CH <sub>3</sub>	CN	H	CH <sub>3</sub>	72-75
53		H	CH <sub>3</sub>	CN	H	CH <sub>3</sub>	98-102
54		H	CH <sub>3</sub>	CN	H	CH <sub>3</sub>	152-157

No. Aryl	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	R <sub>5</sub>	R <sub>6</sub>	M.p (°C)
55		H	CH <sub>3</sub>	CN	H	CH <sub>3</sub>	90-95
56		H	CH <sub>3</sub>	CN	H	CH <sub>3</sub>	
57		H	CH <sub>3</sub>	CN	H	CH <sub>3</sub>	80
58		H	CH <sub>3</sub>	CN	H	CH <sub>3</sub>	125-128
59		H	CH <sub>3</sub>	CN	H	CH <sub>3</sub>	105-107
60	"	H	CH <sub>3</sub>	CN	H	CH <sub>3</sub>	
61		H	CH(CH <sub>3</sub> ) <sub>2</sub>	CN	H	CH <sub>3</sub>	82-84

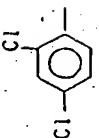
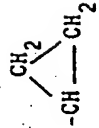

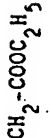
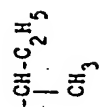
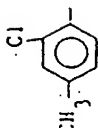

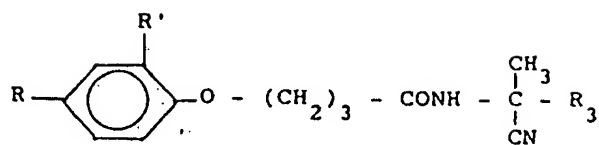
N O. Aryl	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	R <sub>5</sub>	R <sub>6</sub>	M P (°C)
62		H		CN	H	CH <sub>3</sub>	89-94
63	"	CH <sub>3</sub>		CN	H	CH <sub>3</sub>	124-128
64	"	CH <sub>3</sub>		CN	H	CH <sub>3</sub>	
65	"	CH <sub>3</sub>		CN	H	CH <sub>3</sub>	107-110
66		H		CN	H	CH <sub>3</sub>	

TABLE III

Compounds of formula

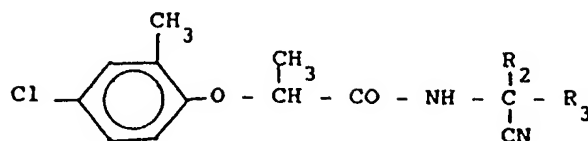


No.	R <sub>3</sub>	R	R'	Mp. (°C)
1	CH(CH <sub>3</sub> ) <sub>2</sub>	Cl	CH <sub>3</sub>	Oil
2	n-C <sub>5</sub> H <sub>11</sub>	Cl	CH <sub>3</sub>	Oil
3	CH(CH <sub>3</sub> ) <sub>2</sub>	CH <sub>3</sub>	Cl	
4	n-C <sub>5</sub> H <sub>11</sub>	CH <sub>3</sub>	Cl	



Table IV

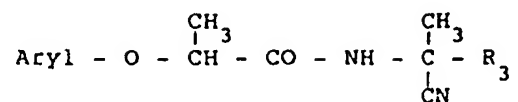
Compounds of formula

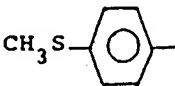
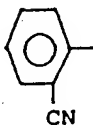
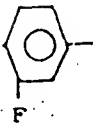
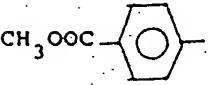
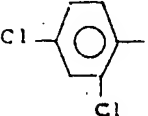


NO.	R <sub>2</sub>	R <sub>3</sub>	M p. [°C]
1	CH <sub>3</sub>	n-C <sub>3</sub> H <sub>7</sub>	71-75
2	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	86-87
3	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	125-126
4	CH <sub>3</sub>	CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	101-102
5	CH <sub>3</sub>	CH <sub>2</sub> OCH <sub>3</sub>	Oil
6	H	CH(CH <sub>3</sub> ) <sub>2</sub>	86-88
7	CH <sub>3</sub>	CH <sub>2</sub> CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	92-94
8	C <sub>2</sub> H <sub>5</sub>	CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	68-70
9	CH <sub>3</sub>	CH(CH <sub>3</sub> )C <sub>2</sub> H <sub>5</sub>	103-109
10	CH(CH <sub>3</sub> ) <sub>2</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>	106-109
11	CH <sub>3</sub>		87-88
12	CH <sub>3</sub>		127-129
13	CH <sub>3</sub>	CH <sub>3</sub>	128-130
14	CH <sub>3</sub>	C(CH <sub>3</sub> ) <sub>3</sub>	110-115
15	H	C <sub>2</sub> H <sub>5</sub>	64-66
16	H	CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>	66-70
17	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	148-152
18	CH <sub>3</sub>	CH <sub>2</sub> SC <sub>2</sub> H <sub>5</sub>	78-82

Table V

Compounds of formula



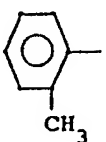
No.	Aryl	R <sub>3</sub>	M p. [°C]
1		CH(CH <sub>3</sub> ) <sub>2</sub>	83-86
2		CH(CH <sub>3</sub> ) <sub>2</sub>	74-76
3		CH(CH <sub>3</sub> ) <sub>2</sub>	71-75
4		CH(CH <sub>3</sub> ) <sub>2</sub>	110-115
5		CH <sub>3</sub>	134-137

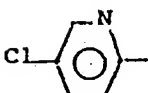
1311240

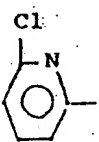
41

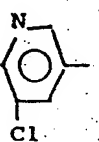
No.	Aryl	R <sub>3</sub>	M p. [°C]
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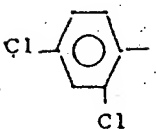
6		CH(CH <sub>3</sub> ) <sub>2</sub>	80-82
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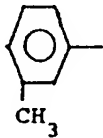

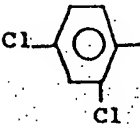
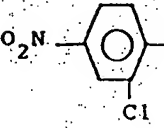
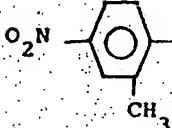
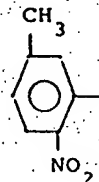
7		CH(CH <sub>3</sub> ) <sub>2</sub>	74-76
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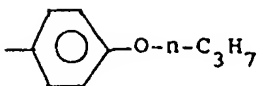
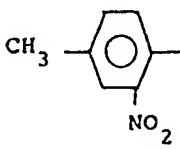
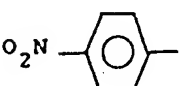
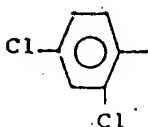
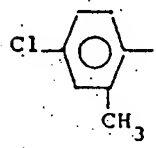

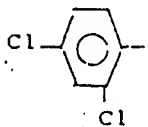

8		CH(CH <sub>3</sub> ) <sub>2</sub>	134-136
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9		CH(CH <sub>3</sub> ) <sub>2</sub>	101-105
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10		CH(CH <sub>3</sub> ) <sub>2</sub>	94-99
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11		C(CH <sub>3</sub> ) <sub>3</sub>	126-130
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No.	Ar <sub>1</sub>	R <sub>3</sub>	M p. [°C]
12		CH(CH <sub>3</sub> ) <sub>2</sub>	85-88
13		CH(CH <sub>3</sub> ) <sub>2</sub>	170-174
14		C <sub>6</sub> H <sub>5</sub>	129-145
15		CH(CH <sub>3</sub> ) <sub>2</sub>	139-142
16		CH(CH <sub>3</sub> ) <sub>2</sub>	124-126
17		CH(CH <sub>3</sub> ) <sub>2</sub>	102-104

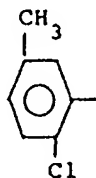
NO.	Aryl	R <sub>3</sub>	Mp. [°C]
18		CH(CH <sub>3</sub> ) <sub>2</sub>	78-80
19		CH(CH <sub>3</sub> ) <sub>2</sub>	87-92
20		CH(CH <sub>3</sub> ) <sub>2</sub>	110-112
21		CH <sub>2</sub> SC <sub>2</sub> H <sub>5</sub>	Oil
22			from 112
23			from 112

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No.	Aryl	R <sub>3</sub>	M p. [°C]
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24

CH(CH<sub>3</sub>)<sub>2</sub>

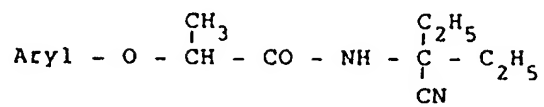
69-71

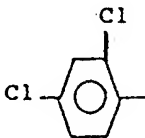
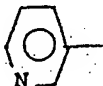
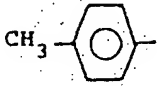
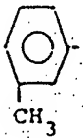
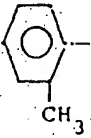
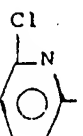
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Table VI

Compounds of formula



N <sup>o</sup> .	Aryl	MP[°C]
1		100-102
2		Oil
3		93-94
4		64-66
5		92-93
6		88-90

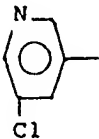
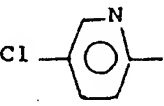
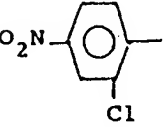
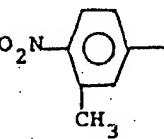
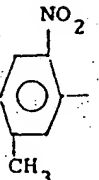
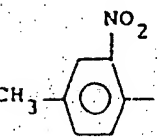
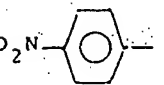
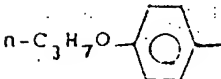
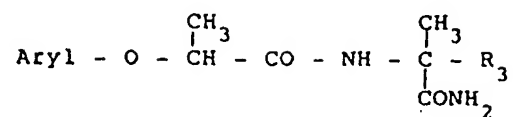
No.	Acyl	Mp[ °C]
7		84-87
8		129-131
9		117-120
10		117-118
11		132-133
12		120-122
13		108-110
14		71-75



Table VII

Compounds of formula



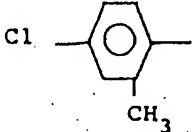
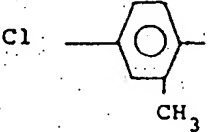
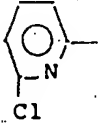
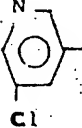
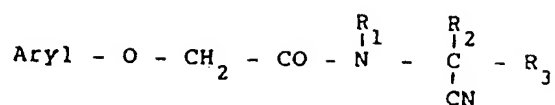
No.	Aryl	R <sub>3</sub>	Mp. [°C]
1		n-C <sub>3</sub> H <sub>7</sub>	100-102
2		n-C <sub>3</sub> H <sub>7</sub>	108-111
3		n-C <sub>3</sub> H <sub>7</sub>	111-113
4		n-C <sub>3</sub> H <sub>7</sub>	115-117

Table VIII

Compounds of formula



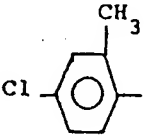
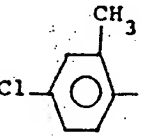
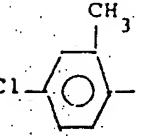

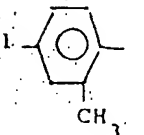
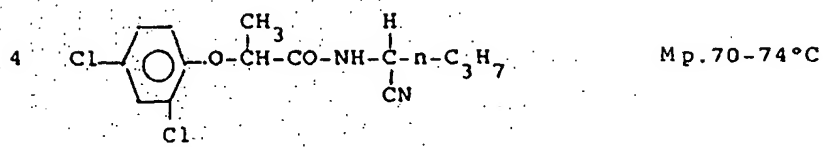
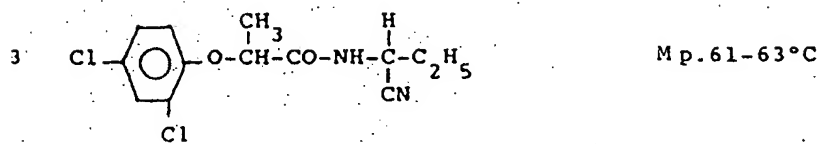
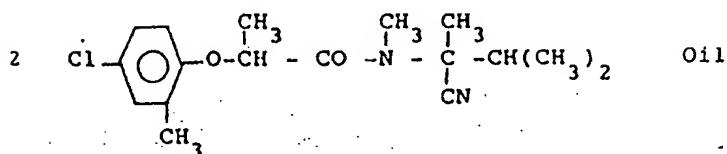
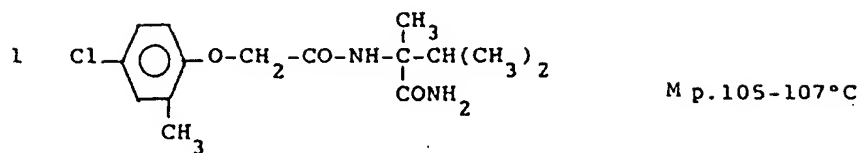
NO.	Aryl	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	M.P. [°C]
1		H	CH <sub>3</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>	100-103
2		H	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	86-88
3		CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>	Oil
4		H	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	50-52
5		H	CH <sub>3</sub>	n-C <sub>5</sub> H <sub>11</sub>	Oil

Table IX

Other compounds according to the invention



## Examples of formulations:

Example I5 Preparation of an emulsifiable concentrate

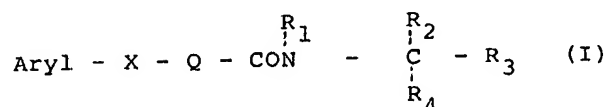
- 5.0 parts by weight of active substance  
according to the invention
- 3.4 parts by weight of epoxidised vegetable oil
- 10 13.4 parts by weight of a combined emulsifier  
of fatty alcohol polyglycol-  
ether and calcium alkylaryl-  
sulphonate
- 40.0 parts by weight of dimethylformamide
- 15 38.2 parts by weight of xylene
- The components are mixed together and, for  
application, diluted with water to give a  
concentration of active substance of 0.01  
20 to 0.1% by weight.

Example IIPreparation of a wettable powder

- 25 10 parts by weight of active substance according  
to the invention
- 3 parts by weight of sodium fatty alcohol  
sulphonate
- 30 5 parts by weight of salts of naphthalene  
sulphonic acid-formaldehyde  
condensate
- 82 parts by weight of kaolin

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

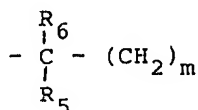
1. A method of preventing or combating Piricularia in rice plants which comprises the application to said plant of one or more compounds of formula (I)



in which Aryl represents a phenyl group, either unsubstituted or mono- to tri-substituted by  $\text{C}_{1-5}$  alkyl groups,  $\text{C}_{1-5}$  alkoxy groups,  $\text{C}_{1-5}$  alkyl- $\text{SO}_n$  groups wherein n represents one of the integers 0, 1 or 2, halogen atoms, groups of formula  $\text{NO}_2$ ,  $\text{CF}_3$ ,  $\text{CN}$ ,  $\text{CH}_3\text{OCH}_2$ ,  $(\text{CH}_3)_2\text{NCH}_2$ ,  $\text{COOalkyl}$ ,  $\text{CONH}_2$  or phenyl groups; a 1- or 2-naphthyl group; an optionally chlorine-substituted 2-, 3- or 4-pyridyl group; or a pyrimidyl or quinolyl group;  $\text{R}_1$  represents a hydrogen atom or a  $\text{C}_{1-5}$  alkyl group or an allyl group;  $\text{R}_2$  and  $\text{R}_3$  independently represent hydrogen atoms,  $\text{C}_{1-6}$  alkyl groups (which may also contain an O or S atom in the chain),  $\text{C}_{3-7}$  cycloalkyl groups, phenyl groups or groups of formula  $\text{CH}_2\text{-COO-(C}_{1-5}\text{ alkyl)}$ ; or  $\text{R}_2$  and  $\text{R}_3$  together represent a group of formula

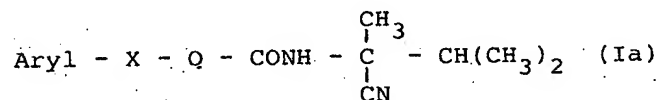
$-(CH_2)_4-$ ,  $-(CH_2)_5-$ , or  $-\underset{\text{CH}_3}{\text{CH}}-(CH_2)_4-$

$R_4$  represents a group of formula CN or  $CONH_2$ ; X represents an oxygen or sulphur atom; and Q represents a group of formula:

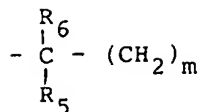


wherein m is one of the integers 0, 1 and 2;  $R_5$  represents a hydrogen atom or a group of formula  $CH_3$  or  $C_2H_5$ ;  $R_6$  represents a hydrogen atom or a group of formula  $CH_3$ ; optionally in the form of racemates or mixtures of the optical isomers or in the form of the pure enantiomers of diastereoisomers.

2. A compound of formula (Ia):



wherein Aryl represents a phenyl group, unsubstituted or mono- to tri-substituted by  $C_{1-5}$  alkyl groups,  $C_{1-5}$  alkoxy groups,  $C_{1-5}$  alkyl- $SO_n$  groups wherein n represents one of the integers 0, 1 or 2, halogen atoms, groups of formula  $NO_2$ ,  $CF_3$ , CN,  $CH_3OCH_2$ ,  $(CH_3)_2NCH_2$ , COOalkyl,  $CONH_2$  or phenyl groups; a 1- or 2-naphthyl group; an optionally chlorine-substituted 2-, 3- or 4-pyridyl group; or a pyrimidyl or quinolyl group; Q represents a group of formula



wherein m is one of the integers 0, 1 and 2; R<sub>5</sub> represents a hydrogen atom or a group of formula CH<sub>3</sub> or C<sub>2</sub>H<sub>5</sub>; R<sub>6</sub> represents a hydrogen atom or a group of formula CH<sub>3</sub>; and X represents an oxygen or sulphur atom; optionally in the form of racemates or mixtures of the optical isomers or in the form of the pure enantiomers or diastereomers.

3. A compound as claimed in claim 2, wherein Aryl is a 4-chlorophenyl, 4-chloro-2-methylphenyl or 2,4-, 3,4- or 3,5-dichlorophenyl group.

4. A compound as claimed in claim 2 or 3, wherein X represents an oxygen atom.

5. A compound as claimed in claim 2 or 3, wherein Q represents a group of formula CH(CH<sub>3</sub>).

6. A compound as claimed in claim 4, wherein Q represents a group of formula CH(CH<sub>3</sub>).

7. 2-(4-Chloro-2-methylphenoxy)-propionic acid-N-[2-cyano-3-methylbut-2-yl] amide.

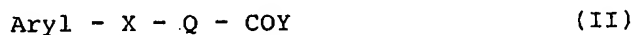
8. A fungicidal composition comprising a compound of formula (I), as defined in claim 2, 3, 6 or 7, optionally in the form of racemates or mixtures of the optical isomers or in the form of the pure enantiomers or diastereomers, together with excipients and/or carriers.

9. A fungicidal composition comprising a compound of formula (I), as claimed in claim 4, optionally in the form of racemates or mixtures of the optical isomers or in the form of the pure enantiomers or diastereomers, together with excipients and/or carriers.

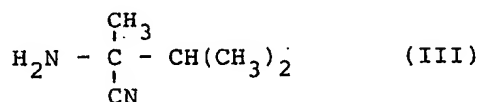
10. A fungicidal composition comprising a compound of formula (I), as claimed in claim 5, optionally in the form of racemates or mixtures of the optical isomers or in the form of the pure enantiomers or diastereomers, together with excipients and/or carriers.

11. A process for preparing compounds of formula (I), as defined in claim 2, 3, 6 or 7, wherein

(a) a compound of formula (II)



wherein Aryl, X and Q are as defined in claim 2, and Y represents a leaving group, is reacted with a compound of formula (III)



or

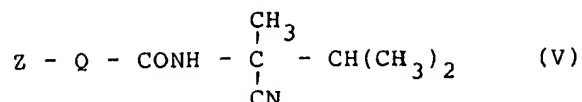
(b) a compound of formula (V):



wherein Aryl and X are as defined in claim 2, and M represents a hydrogen atom, or an alkali metal cation, is reacted with a compound of formula (V)

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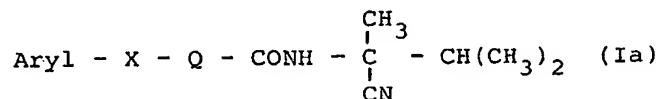




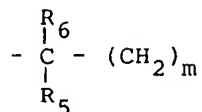
wherein Q is as defined in claim 2 and Z represents a halogen atom or an arylsulphonyloxy group, and, if desired, mixtures of enantiomers obtained are separated by conventional methods into the individual enantiomers or into pairs of diastereomers.

12. A process for the preparation of a fungicidal composition as defined in claim 8, which comprises admixing one or more compounds of said formula (I), as defined in claim 8, with a carrier and/or excipient.

13. A compound of formula (Ia):



wherein Aryl represents a phenyl group, unsubstituted or mono- to tri-substituted by C<sub>1-5</sub> alkyl groups, C<sub>1-5</sub> alkoxy groups, C<sub>1-5</sub> alkyl-SO<sub>n</sub> groups wherein n represents one of the integers 0, 1 or 2, halogen atoms, groups of formula NO<sub>2</sub>, CF<sub>3</sub>, CN, CH<sub>3</sub>OCH<sub>2</sub>, (CH<sub>3</sub>)<sub>2</sub>NCH<sub>2</sub>, COOalkyl, CONH<sub>2</sub> or phenyl groups; a 1- or 2-naphthyl group; an optionally chlorine-substituted 2-, 3- or 4-pyridyl group; or a pyrimidyl or quinolyl group; Q represents a group of formula



wherein m is one of the integers 0, 1 and 2; R<sub>5</sub> represents a hydrogen atom or a group of formula CH<sub>3</sub> or C<sub>2</sub>H<sub>5</sub>; R<sub>6</sub> represents a hydrogen atom or a group of formula CH<sub>3</sub>; and X represents an oxygen or sulphur atom; optionally in the form of racemates or mixtures of the optical isomers or in the form of the pure enantiomers or diastereomers, for use in preventing or combatting fungal infections in plants.

14. A compound of claim 13, wherein Aryl is a 4-chlorophenyl, 4-chloro-2-methylphenyl or 2,4-, 3,4- or 3,5-dichlorophenyl group, for use in preventing or combatting fungal infections in plants.

15. A compound of claim 13, wherein X represents an oxygen atom for use in combatting fungal infections in plants.

16. A compound of claim 14, wherein X represents an oxygen atom for use in combatting fungal infections in plants.

17. A compound of claim 13, wherein Q represents a group of formula CH(CH<sub>3</sub>) for use in combatting fungal infections in plants.

18. A compound of claim 14, wherein Q represents a group of formula CH(CH<sub>3</sub>) for use in combatting fungal infections in plants.

19. A compound of claim 15 or 16, wherein Q represents a group of formula CH(CH<sub>3</sub>) for use in combatting fungal infections in plants.

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20. 2-(4-Chloro-2-methylphenoxy)-propionic acid N-[2-cyano-3-methylbut-2-yl)-amide for use in combatting fungal infections in plants.

21. A compound of claim 13, 14, 15, 16, 17, 18 or 20, for use in preventing or combatting Piricularia in rice plants.

22. A compound of claim 19, for use in preventing or combatting Piricularia in rice plants.

23. A method of claim 1, wherein said compound of formula (I) is a compound of formula (Ia), as defined in claim 2.

24. A method of claim 23, wherein Aryl is a 4-chlorophenyl, 4-chloro-2-methylphenyl or 2,4-, 3,4- or 3,5-dichlorophenyl group.

25. A method of claim 23, wherein X is an oxygen atom.

26. A method of claim 23, wherein Q is a group of formula  $\text{CH}(\text{CH}_3)$ .

27. A method of claim 24, wherein X is an oxygen atom.

28. A method of claim 24, wherein Q is a group of formula  $\text{CH}(\text{CH}_3)$ .

29. A method of claim 25 or 27, wherein Q is a group of formula  $\text{CH}(\text{CH}_3)$ .

30. A method of claim 1, wherein said compound of formula (I) is 2-(4-Chloro-2-methylphenoxy)-propionic acid-N-[2-cyano-3-methylbut-2-yl)amide.

#8 02/12/92



